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Hazardous Air Pollutants (HAPs) Analysis in Coating Materials via Gas Chromatography (GC)

by Philip H. Patterson
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Hazardous Air Pollutants (HAPs) Analysis in Coating Materials via Gas Chromatography (GC)

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Abstract

This technical report covers the analytical work performed on the U.S. Army Research Laboratory (ARL) project entitled "Analysis of Class I Ozone Depleting Chemicals and Aromatic Solvents in Coating Related Materials Using Gas Chromatography." General background information is provided and final results of several GC analyses for solvent content are tabulated and discussed.

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1. INTRODUCTION

The analysis of solvent content in coating materials has always been an important determination when evaluating quality control of a given product formulation. However, with every tightening air pollution regulation, these analyses become even more critical in assuring product compliance to the proper volatile organic compound (VOC) emissions level.

Most recently, the Environmental Protection Agency (EPA) has amended the 1990 Clean Air Act to regulate the emissions of 189 specific toxic pollutants. Several of these targeted compounds, also known as Hazardous Air Pollutants (HAPS), are commonly used as solvents in many industrial and military coatings. Among the list of coating solvents, which are now classified as HAPs, are methyl ethyl ketone, methyl iso-butyl ketone, xylene, toluene and ethylbenzene. Noteworthy is the fact that these volatile solvents can comprise as much as 30–40%. by weight of the Army's primary camouflage topcoat, MIL-C-46168 [1]. Further restrictions of solvent content allowable in Army coating materials were established under Section 326 of the National Defense Authorization Act of 1993. This Act specified the elimination of Class I ozone depleting chemicals (i.e., carbon tetrachloride and 1,1,1 trichloroethane) in products or standards listed in defense procurement contracts. Therefore, as these coatings are reformulated to conform to the HAPs content restrictions, the methodology to detect these compounds must also improve.

Currently, analytical procedures for determining solvent content are found in Federal Standard Test Method 141 (FSTM-141). For example, FSTM-141 #7356 "Solvent Content of Enamels and Enamel Thinners (Via Gas Chromatography [GC])" is a commonly referenced method cited in many Army coating specifications. This particular method calls for the use of a GC equipped with an 8-ft stainless steel packed column (35% N, N-bis (2-cyanoethyl) formamide on 60–80 mesh chromosorb P support). This specialized, highly polar column is used for the determination of aromatic hydrocarbons (i.e., toluene, ethylbenzene, xylene) found in the coating solvent blend.

Although the method is reliable, analysis time is lengthy. A single determination takes

approximately 45–50 min to complete; and, although this column is well suited for aromatic hydrocarbon analyses, it is not well suited for determining the presence of other classes of VOCs. Additionally, today's new GCs are not designed for using the larger, outdated, packed-column technology. For these reasons, a revision in methodology, using an updated system, needs to be developed to increase analytical efficiency.

2. METHOD

2.1 Instrumentation. For this study, a Hewlett-Packard 5890 Series II GC with a flame ionization detector (FID) was used for the determinations. Integrated to the GC was a Hewlett-Packard G127A Chemstation loaded with application software to control instrument operation and data collection (chromatograms).

For the initial phase, a J&W Scientific DB-624 fused-silica megabore column (1.5 M x 15 m x 0.53 mm) was selected for the HAPs GC analysis [2]. This general purpose, easily installed column was chosen as a practical alternative to the currently used 8-ft stainless steel packed column. Also, because of the column's DB-624 stationary phase (a cross-linked diphenyl dimethyl polysiloxane polymer is relatively nonpolar), the separation of components occurs primarily due to dispersive effects. This means that the election order of the detected compounds is determined in large part by the difference in boiling points (values that are readily referenced and easy to compare).

However, it was foreseen that if more complex mixtures of HAPs were encountered in the coating sample, a more efficient capillary column would be necessary to obtain adequate separations. For this reason, in the second phase of the study, a more specialized column was evaluated. Selected was a J&W Scientific DB-624 fused-silica megabore column (3.0 M x 30 m x 0.53 mm). The column has been previously applied in purge and trap analysis of volatile priority pollutants (EPA Methods 601/602 and 1624) and in the trace analysis of solvent contamination in pharmaceuticals [3,4]. The increased polarity and film thickness of the column's stationary phase (a cyanopropylphenyl-dimethyl polysiloxane polymer) is expected to increase retention of even the

stationary phase (a cyanopropylphenyl-dimethyl polysiloxane polymer) is expected to increase retention of even the most volatile of the HAPs compounds. Additionally, this size column provides for larger sample capacity and better peak resolution for the more concentrated solvent components.

2.2 Sample Preparation. In this GC study, the most commonly encountered classes of HAPs (ketones, aromatics, and chlorinated hydrocarbons) were chosen to test the selectivity of each of the megabore columns. Retention times were verified by using known reference materials and internal standards. All chemicals used in the analysis were American Chemical Society (ACS) reagent-grade purity or higher.

For the DB-5 screening column, the concentrations of the reference materials were 2% (v/v) in dichloromethane. For the DB-624 analytical column, concentrations ranged from 10% to 0.25% (wt/v). The coating samples analyzed on this column were prepared by centrifuging out the pigments and then diluting a portion of the vehicle to obtain the proper analyte concentrations. The pigments were removed to avoid plugging of the GC syringe needle. A HAPs compliant thinner, Exxon's Aromatic 150, was also analyzed as a "blank" determination. Aliquots of the test solutions were manually injected into the GC using a standard borosilicate glass syringe with a 26-gauge needle.

3. RESULTS/DISCUSSIONS

The results (chromatograms) of the initial GC screenings for each group of HAPs compounds are shown in Figures 1-3. GC conditions are noted on each of the figures. As expected, the DE-5 megabore column did well in separating the compounds with different boiling points within the same chemical class. However, upon closer inspection of retention times, it is apparent that resolution would be compromised if complex mixtures were encountered. For this reason, a series of mixed HAPs solutions of varying concentrations were analyzed on the DB-624 analytical column. Figure 4 shows the results of analysis for the 10% (wt/v) solution. An internal standard, n-butylacetate, was added at the same approximate concentration level.

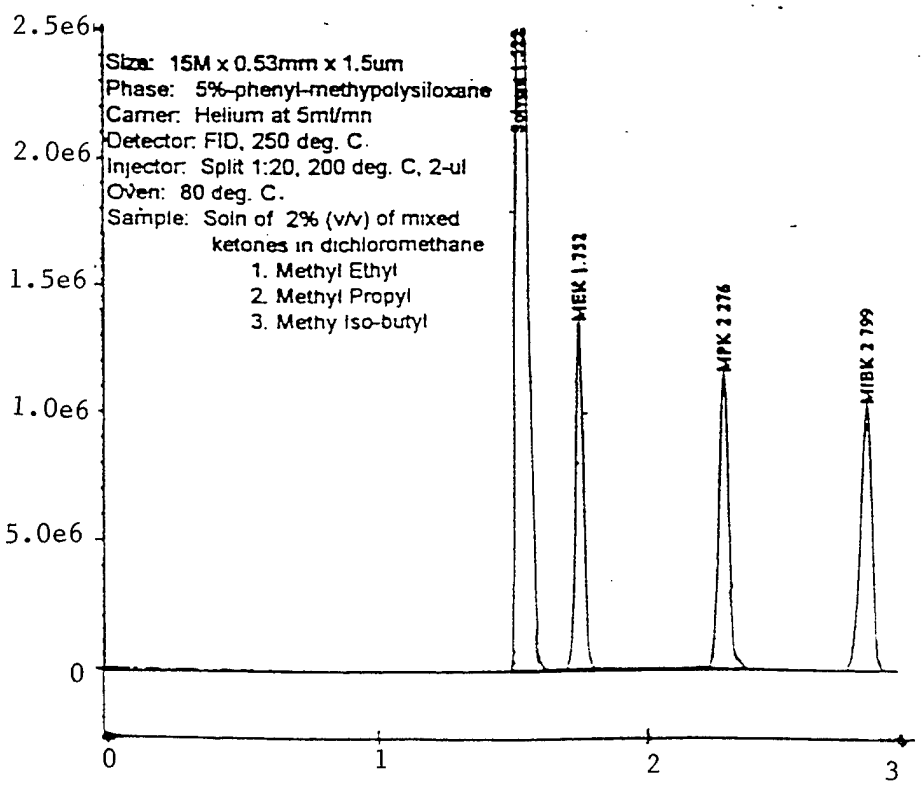

Figure 1. GC analysis of ketones.

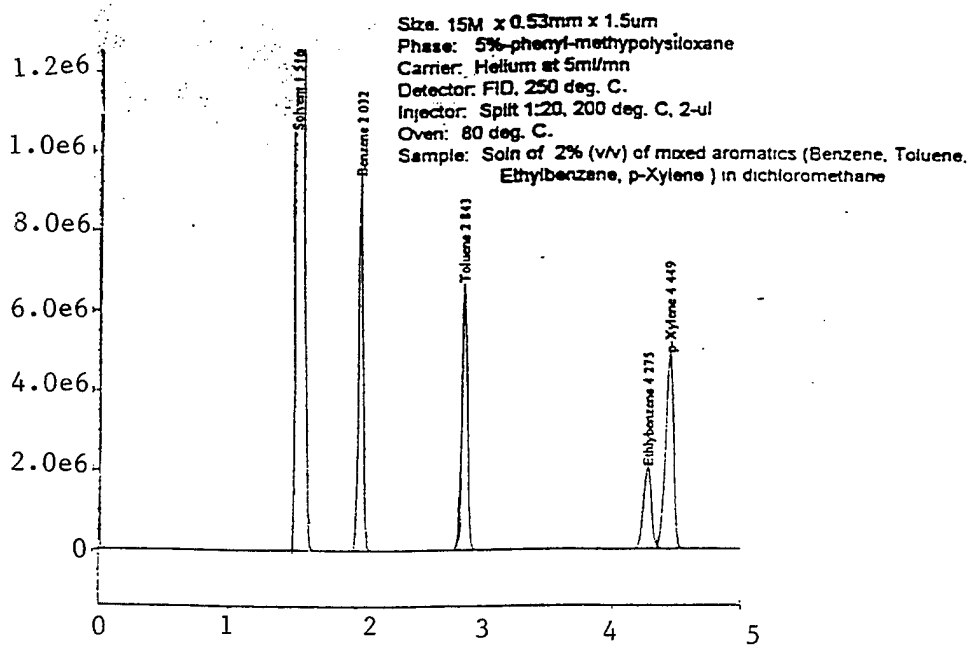

Figure 2. GC analysis of aromatics.

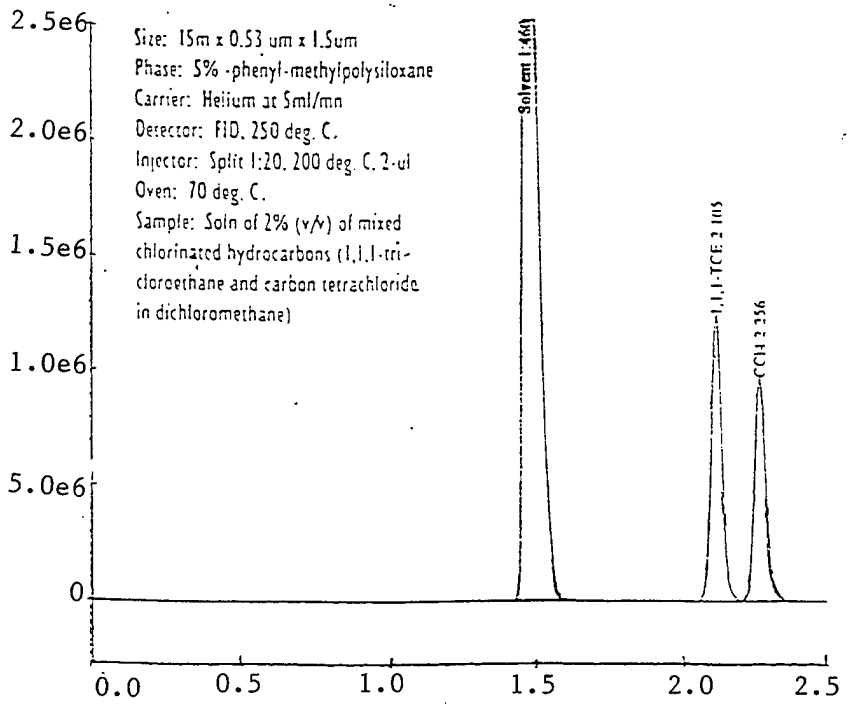

Figure 3. GC analysis of chlorinated hydrocarbons.

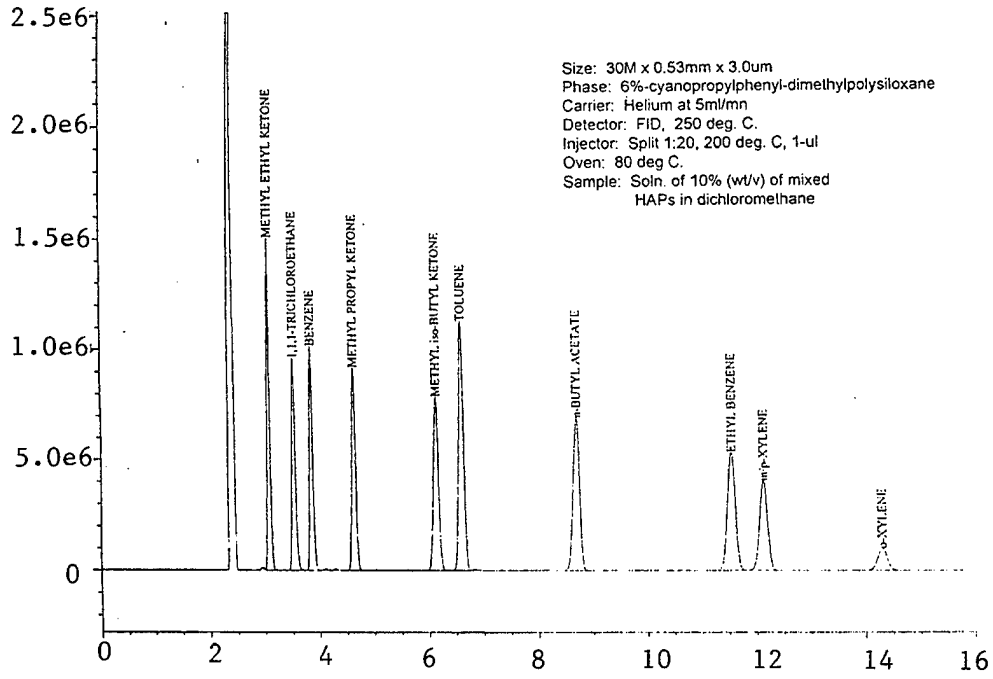

Figure 4. GC analysis of mixed HAPs.

Table 1. Relative Retentions of Selected HAPs on DB-624 Megabore Column

Compound	Relative Retention Time (min)
Methyl Ethyl Ketone	0.35
1, 1, 1 Trichloroethane (1, 1, 1 TCA)	0.40
Benzene	0.44
Methyl Propyl Ketone	0.53
Methyl Iso-Butyl Ketone	0.70
Toulene	0.76
N-Butyl Acetate, Internal STD	1.00
Ethylbenzene	1.32
M/P-Xylene	1.39
O-Xylene	1.64

As with the DB-5 column, elution order is largely determined by boiling point differences. Also, the variances in relative retention times are large enough to make a preliminary identification of each individual HAP. Relative response factors remained constant throughout the established concentration range. The correlation coefficients for the GC internal standard calibration runs were 0.99 or better. Table 2 lists a few of the HAPs standard results.

Table 2. Linearity of HAPs Determination via GC/FID

HAPs Compound	Method	Concentration Range (wt/v)	Correlation Coefficient
O-Xylene	Internal Std	10–0.25%	0.9979
Methyl Iso-Butyl Ketone	Internal Std	10–0.25%	0.9993
1, 1, 1 Trichloroethane (1, 1, 1 TCA)	Internal Std	10–0.25%	0.9910

To determine repeatability at a given concentration, multiple injections of the various HAPs solutions were made. Integrations by peak area were determined for each component and then ratioed to the internal standard peak area.

The HAPs solutions at 1% concentrations produced the most reliable results, with duplicate means differing by less than 1.5% for all of the tested compounds. Therefore, this analyte concentration was chosen for sample preparation prior to analysis. It should be noted that the actual regulatory limit of total HAPs content, although not firmly established, may be lower than this concentration.

The coating samples chosen for the HAPs analysis represents a broad range of MIL-SPEC materials. The most commonly encountered primers, topcoats, and thinners were analyzed in this study. Table 3 summarizes the results of the GC analysis. The detected value is the mean of duplicate determinations and has been adjusted to account for pigment content. The theoretical value is a reported quantity as derived by the manufacturer.

For the MIL-C-46168 coating, the internal standard (n-butyl acetate) was substituted with iso-butyl iso-butyrate (relative retention time = 1.88). This was necessary since n-butyl acetate was a component of the coating's solvent mixture. For samples with late eluting compounds (high boilers), the GC temperature was raised to 2,250° C for 15 min to avoid the appearance of "ghost" peaks in subsequent runs; this is quite common in thinners where the composition is often a blend of these compounds.

The results, as shown in Table 3, indicate that the concentration level of a given HAP compound in any of the selected coating materials can be readily distinguished. Although the quantitation could be improved, the method does show values closely agreeing, even when there is a tenfold difference in the individual HAPs components (i.e., MIL-P-53022).

Although not encountered in this study, injection repeatability may be affected by a buildup of unvaporized material in the injection liner. Therefore, a regular maintenance check of this component is suggested.

Table 3. HAPs Analysis of Coating Materials

Coating Type	HAP	% WT. (Theoretical/Detected)
MIL-P-53022	Toulene Xylene(s)	(1.4/1.6) (0.10/<0.25)
MIL-C-53039	Methyl Iso-Butyl Ketone Toulene Xylene	(5.8/3.8) (3.9/3.6) (16.5/16.9)
MIL-C-46168	Methyl Ethyl Ketone Toulene	(5.8/6.9) (6.5/7.2)
MIL-C-4556	Xylene(s)	(0.8/1.0)
MIL-E-11195	Methyl Ethyl Ketone Methyl Iso-Butyl Ketone Xylene(s)	(0.9/1.5) (11.0/12.6) (11.0/10.5)
Aromatic 150 Thinner (Blank)	No HAPs Detected	
Aromatic 150 Thinner (Spiked W/1% Benzene) (0.1% 1, 1, 1 TCA)	Benzene 1, 1, 1 TCA	(1.0/0.9) (0.1/<0.25)

4. CONCLUSIONS

For initial screening of HAPs found in coating solvents, the DB-5 megabore column (15 m x 0.53 mm) can be successfully applied for simple mixtures. Separation of compounds within the same chemical class was easily performed in a very short period of time (less than 5 min).

For more complex sample mixtures, or when the HAPs content level must be determined, the DB-624 megabore column provides the necessary increase in efficiency. However, the use of this high-performance column also leads to an increase in analysis time to approximately 20 min, although this is still a reasonable length compared to the packed-column methodology.

Sample preparation is relatively easy and straightforward. Samples are introduced into the GC as a simple "dilute and shoot" technique. In this study, a wide array of coating materials were analyzed with no particular problems with sample preparation.

Lastly, both of these durable megabore columns are readily available from several vendor sources and are easy to use by any chromatographer, even if the experience is limited to packed-column technology.

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5. REFERENCES

1. Department of the Army. "Coating, Aliphatic Polyurethane, Chemical Agent Resistant." Military Specification: MIL-C-46168D, 21 May 1987.

2. Patterson, P., and W. Lum. "Analysis of Hazardous Air Pollutants (HAPS) in Coating Solvent Via Capillary Gas Chromatography." ARL-MR-321, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, p. 4, 1996.

3. Decker, D. "DB-624 Megabore Application Guide." Separation Times, vol. 5, no. 3, p. 7, 1992.

4. Buicker, A., J. Thomasson, and E. M. Shorts. "Capillary Columns for Btex Analysis in Pharmaceutical Products." Journal of Pharmaceutical Technology, vol. 21, pp. 240–244, 1981.

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